

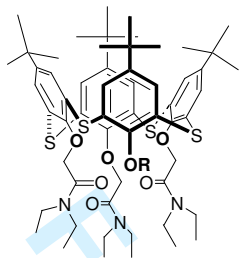
# **Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted Thiacalix[4]arenes**

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Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted Thiacalix[4]arenes

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TC1 R = H  
TC2 R = nPropyl  
TC3 R = Etylacetate

New thiacalix[4]arenes appended with three amide functions have been prepared. The complexation ability of these ligands towards various metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Pd}^{2+}$ ;  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) has been investigated by UV-vis absorption.

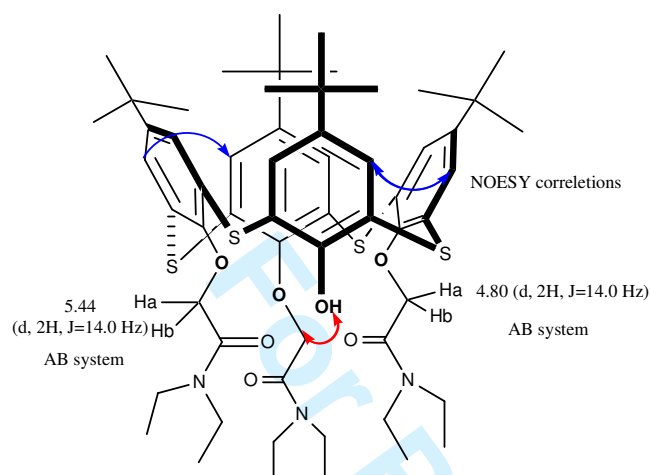


Figure 1. Conformational analysis of TC1.

$\text{CH}_3\text{CN}$  resulting from additions of  $\text{Pb}(\text{NO}_3)_2$  ( $5 \cdot 10^{-4}$  M in acetonitrile/water, 3v/v).

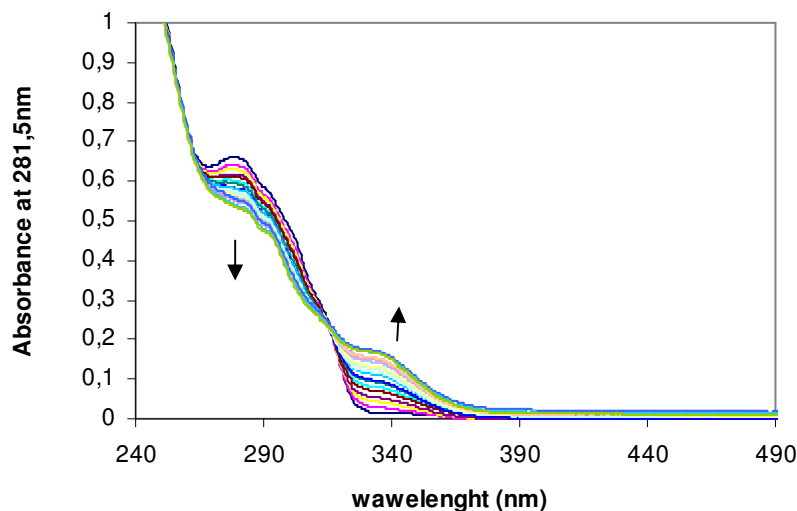
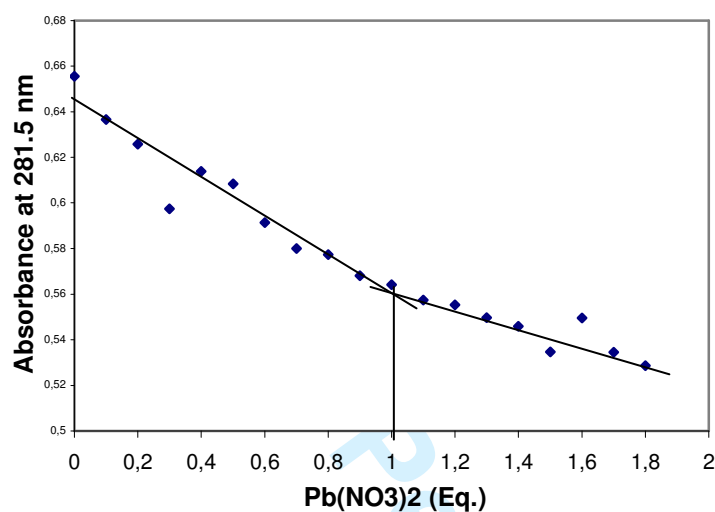
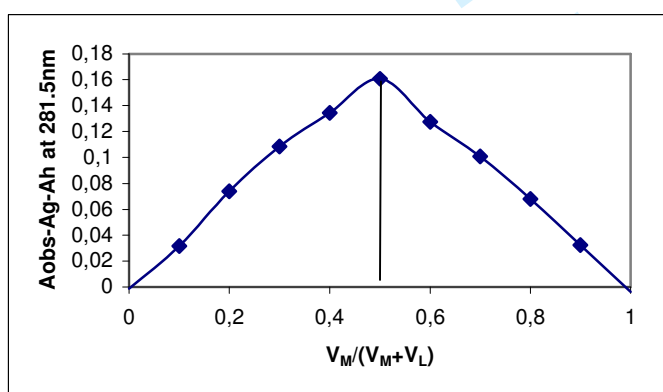


Figure 2. Changes in the absorbance spectrum of a  $5 \cdot 10^{-5}$  M solution of ligand **TC1** in  $\text{CH}_3\text{CN}$  resulting from additions of  $\text{Pb}(\text{NO}_3)_2$  ( $5 \cdot 10^{-4}$  M in acetonitrile/water, 3v/v).

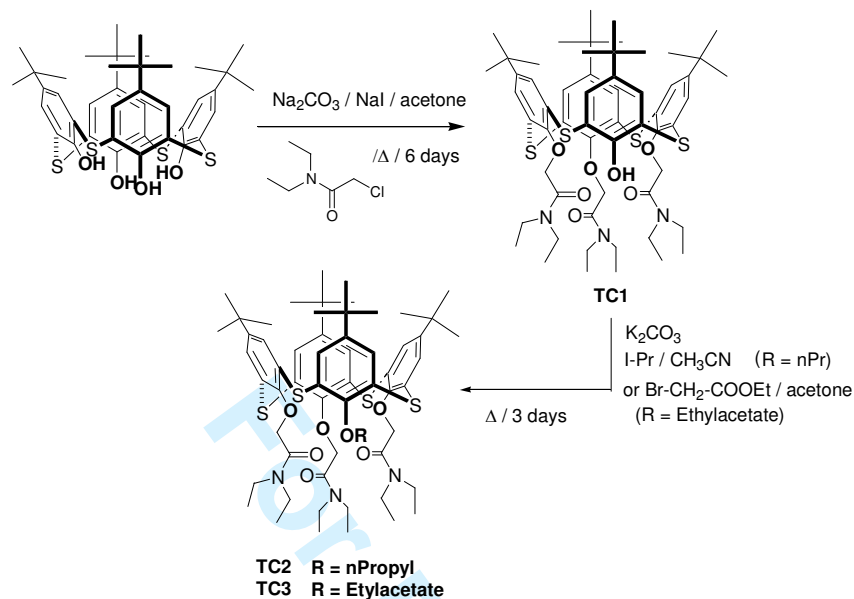


(a) Mole ratio method of Pb<sup>2+</sup>-TC1 mixture



(b) Job plot of the titration of Pb<sup>2+</sup> with TC1.

Figure 3. Determination of the stoichiometry of Pb-ligand Complex



Scheme 1. Synthesis of triamide ligand derivatives.

*Supramolecular Chemistry***Synthesis and Complexation Properties Towards Metal Ions of New Tri-substituted  
Thiacalix[4]arenes**

**Abstract.** New thiacalix[4]arenes appended with three amide functions have been prepared. Their conformations have been solved thanks to  $^1\text{H}$  NMR 2D COSY and NOESY. The complexation ability of these ligands towards various metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Pd}^{2+}$ ;  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) has been investigated by UV-vis absorption and the stoichiometry of the metal-ligand complexes was determined.

**Keywords:** thiacalix[4]arene, synthesis, conformation, metal complexation.

**Introduction**

Toxic heavy metals like copper, mercury, lead, nickel or cadmium can have a serious impact on the aqueous environment. So, detection and treatment of these toxic metal ions still remain an important topic. In this field, calixarenes, the well known cyclic oligomers of *p*-substituted phenols and formaldehyde, have attracted increased interest. Since the conventional

calix[4]arenes have poor coordination ability towards metal ions, chemical modifications have taken place by introducing functional groups having metal-binding ability. Recently, a new class of macrocycles named thiacalixarenes has emerged. The presence of sulphur atoms (which possess lone pairs and vacant 3d orbitals) instead of methylene bridges opens new possibilities, especially in the field of metal complexation. The parent thiacalix[4]arene was found to extract a wide range of transition metal ions from water, in contrast to classical calix[4]arene (1). From many years, our group was interested in metal ions complexation and extraction (2-4). Hence, we have previously reported the synthesis of a thiacalix[4]arene with tetra-amide functions at the lower rim (4). Extraction experiments have evidenced a remarkable binding ability of this ligand towards a wide range of metal cations.

With the aim of supplementing this study, we wondered about the role of the number of chelating groups. The lower rim functionalization of thiacalix[4]arene is becoming better understood following the work of Lhotak (5,6) and Yamamoto (7). A few articles reports the odd functionalisation of thiacalixarenes. Among them, for example the trimethylation of the hydroxyls of thiacalix[4]arene (5) was described (5) using  $K_2CO_3$  in acetonitrile.

In this paper, we describe the preparation of thiacalix[4]arenes substituted with tri-amide functions at the lower rim. The complexation ability of these new ligands towards various metal ions has been investigated by UV-vis titration. The goal of this work is to dispose of a macrocycle which could be grafted on a surface without losing its complexation properties.

### Preparation and characterization of the ligands

The synthetic route for the ligands **TC1-3** is depicted in Scheme 1. The O-alkylation of the lower rim of the parent *p-tert*-butylthiacalix[4]arene was achieved by action of  $Na_2CO_3$  (3eq.) in acetone in presence of NaI, followed by 2-chloro-*N,N*-diethylacetamide. The reaction was refluxed three days and the crude product was purified by chromatography on silica gel to



afford the pure **TC1**.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **TC1** in  $\text{CDCl}_3$  showed the presence of the expected tri-amide derivative. However, it was difficult to determine the conformation of **TC1**. To complete the structural analysis, 2D COSY and NOESY experiments were performed. The  $^1\text{H}$  NMR shows two doublets and one singlet for the  $\text{O}-\text{CH}_2-\text{C}=\text{O}$  signal. The 2D COSY confirms the presence of an AB system for two  $\text{O}-\text{CH}_2-\text{C}=\text{O}$  groups and a singlet for the third one (Figure 1). This AB system results from the rigidity of the calixarene conformation and of the prochirality of two of the  $\text{CH}_2$  groups. The 2D NOESY shows correlation spots between the aromatic hydrogens of neighboring phenyl moieties. A correlation spot is also present between one  $\text{O}-\text{CH}_2-\text{C}=\text{O}$  group (corresponding to the singlet signal) and the  $\text{OH}$  function (Figure 1). With the sight of these results, we can conclude that the tri-substituted thiacalix[4]arene **TC1** adopts a cone conformation in solution. Then the derivatization of the thiacalixarene **TC1** was researched to establish the influence of the substitution of the phenolic group on the complexation of metallic cations. At first **TC1** was alkylated with 1-iodopropane in refluxing acetonitrile in the presence of  $\text{K}_2\text{CO}_3$  as a base. The desired product **TC2** bearing three amide group and one propyl group was obtained after chromatographic separation. **TC1** was also alkylated with ethylbromoacetate in refluxing acetone in the presence of  $\text{K}_2\text{CO}_3$  as a base. The desired product **TC3** bearing three amide group and one ethylacetate group was also obtained after chromatographic separation. The compounds **TC2** and **TC3** were identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and, ES-MS. The NMR analysis showed that the cone conformation was conserved for the two macrocyclic derivatives.

### Complexation study

The UV-vis spectra of **TC1-3** show characteristic bands between 290 and 340 nm in  $\text{CH}_3\text{CN}$  /  $\text{H}_2\text{O}$  (3v/v). Complexation properties of **TC1-3** were studied towards various metal salts

( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) by UV-vis titrations. In all cases, upon addition of metal cations solutions to a solution of **TC1-3**, spectra undergo clear changes and show the presence of isobestic points indicating the existence of complex species. The addition of aliquots of  $\text{Pb}^{2+}$  (from 0.2 to 1 equivalent) to a solution of **TC1** in a mixture of acetonitrile and water (3v/v) led to a decrease in the absorption bands at 280 nm and to the appearance of a new absorption band centred at 335.5 nm that is characteristic of a MLCT (Metal-Ligand Charge Transfer) band between  $\text{Pb}^{2+}$  and the nitrogen and oxygen atoms of the amide functions on the macrocycle (Figure 2). The isobestic point centred at 315.5 nm shows the formation of a new complex. Similar effects were observed upon addition of  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$  and  $\text{Cu}^{2+}$ . Upon addition of cations solutions, we can observe in all cases a hypsochromic effect of the band at 285 nm and MLCT bands.

The stoichiometry of metal-ligand (M-L) complexes was determined both by the molar ratio (8) and the Job plot (9) methods (Figure 3). The results are given in Table 1. They indicate a 1:1 stoichiometry for five complexes ( $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ) in accordance with the literature data (10). We observed the formation of  $\text{M}_x\text{-L}_y$  complexes with  $\text{Hg}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . It should be outlined that no complexation was observed for **TC1** with  $\text{Hg}^{2+}$ . For comparison, the complexation of mercury salts by the tetra-amide-thiacalix[4]arene derivative was studied: this macrocycle does not retain  $\text{Hg}^+$  (11) ions but a complex is obtained between  $\text{Hg}^{2+}$  ions and the receptor in acetonitrile as solvent (5). Complexation properties of **TC2** are reported in Table 1. ML type complexes are obtained for  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$ . Compared with the ligand **TC1**, we can highlight the formation of a monovalent complex with  $\text{Zn}^{2+}$ . No complexation occurs with  $\text{Hg}^+$  whereas the addition of  $\text{Hg}^{2+}$  ions in a solution of **TC2** leads to the formation of a multivalent complex. The ligand **TC3**, bearing an ester group instead of a propyl chain, affords ML type complexes with  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Pd}^{2+}$ . A  $\text{ML}_2$  type complex is observed with  $\text{Ag}^+$ .

The stability constants  $K$  are defined as the concentration ratio [Eq. (1)] :

$$(1) \quad K = \frac{[ML]}{[M][L]}$$

$K$  can be correlated to the change in absorbance due to the formation of the  $ML$  complex.

Further modifications of the Benesi –Hildebrand method (12) result in an equation where a double reciprocal plot can be made with  $1/\Delta A$  as a function of  $1/[M]$  [Eq.(2)] :

$$(2) \quad \frac{1}{\Delta A} = \left[ \frac{1}{\Delta \varepsilon [L]_0 K} \right] \left[ \frac{1}{[M]} \right] + \frac{1}{\Delta \varepsilon [L]_0}$$

The logarithms of the stability constants (Log  $K$ ) are collected in Table 2. Values of the stability constants seem to indicate that the cation  $Cd^{2+}$  is strongly complexed with ligand **TC1** undoubtedly because of its great affinity for N and O atoms. **TC2** and **TC3** ligands exhibit affinity in the same range for all metal cations. This indicates that the introduction of an ester function instead of a propyl chain does not affect their binding ability. These results also show that it will be possible to introduce on the ligand **TC1**, a spacer with a terminal function as silane or thiol allowing the grafting on a surface without loss of recognition. On this way **TC1** is more interesting than the thiacalixarene with the four tetra-amide functions.

## Conclusion

New thiacalix[4]arene derivatives appended with three amide functions have been prepared and their conformation described. The complexation ability of these ligands towards various metal ions has been investigated by UV-vis absorption. These receptors exhibit similar

complexation ability and selectivity except for  $\text{Cd}^{2+}$ . The main difference is observed for mercury salts. **TC1** binds selectively  $\text{Hg}^+$  (*versus*  $\text{Hg}^{2+}$ ), whereas **TC2** forms selectively a multivalent complex with  $\text{Hg}^{2+}$  (*versus*  $\text{Hg}^+$ ) and **TC3** gives only a ML type complex with  $\text{Hg}^{2+}$ . It seems that the number of amide groups doesn't play a crucial role (4), but the presence of an OH function directs the selectivity towards the complexation of  $\text{Hg}^+$ . The extraction ability of **TC1** derivative for noble metals such as  $\text{Pd}^{2+}$  and  $\text{Au}^{3+}$  has been investigated by means of liquid-liquid extraction experiments (13). It has been observed that a similar behaviour is exhibited in the case of gold for the ligand **TC1** and for the thiacalix[4]arene tetra-amide. In the case of palladium, the extraction efficiency increases with **TC1** ligand. Moreover, the new **TC1** derivative has been successfully used as carrier for  $\text{Pd}^{2+}$  and  $\text{Au}^{3+}$  transport in a SLM (supported liquid membrane).

## Experimental section

**General methods.** Solvents were purified and dried by standard methods prior to use. All reactions were carried out under nitrogen. Column chromatography was performed with silica gel 60 (0.040-0.063 nm). Melting points are uncorrected.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained at 300.13 and 75 MHz ( $\text{CDCl}_3$ , TMS as internal standard, chemical shifts in ppm, J in Hertz). Mass spectra were obtained by electrospray technique (positive mode).

**5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-*N,N*-diethylaminocarbonyl-28-hydroxythiacalix[4]arene **TC1**** (cone conformer). To a solution of 0.4g ( $5.55 \cdot 10^{-4}$  mol) of *p*-*tert*-butylthiacalix[4]arene and 0.176g ( $1.66 \cdot 10^{-3}$  mol) of  $\text{Na}_2\text{CO}_3$  in acetone (60 mL), under nitrogen flux, was added 0.25g ( $1.66 \cdot 10^{-3}$  mol) of NaI and 0.24 mL ( $1.66 \cdot 10^{-3}$  mol) of 2-chloro-*N,N*-diethylacetamide. The mixture was refluxed for three days. The solvent was removed under vacuum. To the residue was added  $\text{CHCl}_3$  (40 mL). The organic layer was sepa-

rated, washed with water ( $2 \times 20$  mL) and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was purified by chromatography on silica gel (0.04-0.063 mm from Merck; eluted with heptane /  $\text{CHCl}_3$  1:1) to afford pure **TC1** (286 mg, 48 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 9.18 (s, H, Ar-OH), 7.53 (s, 2H, Ar-H), 7.38 (s, 2H, Ar-H), 7.12 (s, 4H, Ar-H), 5.54 (s, 2H, Ar-O- $\text{CH}_2$ -CO-), 5.44 (d, 2H (AB system),  $^2J$  = 14.0, Ar-O- $\text{CH}_2$ -CO-), 4.82 (d, 2H (AB system),  $^2J$  = 14.0, Ar-O- $\text{CH}_2$ -CO-), 3.51-3.34 (m, 12H, -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 1.32-0.94 (m, 54H, Ar-C( $\text{CH}_3$ ) $_3$ , -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 168.70 and 167.72 (- $\text{CH}_2$ -CO-N-), 157.28 and 157.83 (ArC-O), 147.12, 145.57 et 142.03 (Ar-C( $\text{CH}_3$ ) $_3$ ), 135.53, 134.48 and 133.37 (ArC-H), 129.42 and 122.14 (ArC-S), 72.71 and 69.39 (Ar-O- $\text{CH}_2$ -CO-), 41.37 and 40.17 (-CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 34.39 (Ar-C( $\text{CH}_3$ ) $_3$ ), 31.67 (Ar-C( $\text{CH}_3$ ) $_3$ ), 14.82 and 13.56 (CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ). ES-MS. (positive mode) : mass ( $m/z$ ) = 1060  $[\text{M}+\text{H}]^+$ , 1082.4  $[\text{M}+\text{Na}]^+$ . Mp = 138 °C.

**5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-27-*N,N*-diethylaminocarbonyl-28-propyloxythiacalix[4]arene TC2** (cone conformer). To a solution of 0.1 g (0.094 mmol) of **TC1** and 0.065 g (0.471 mmol) of  $\text{K}_2\text{CO}_3$  in acetonitrile (5 mL), under nitrogen flux, was added 0.092 mL (0.943 mmol) of 1-iodopropane. The mixture was refluxed for three days. The solvent was removed under vacuum. To the residue was added  $\text{CHCl}_3$  (10 mL) and an aqueous solution of HCl 1N (10 mL). The organic layer was separated, washed with water ( $3 \times 10$  mL) and dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was purified by chromatography on silica gel (0.04-0.063 mm from Merck; eluted with heptane /  $\text{CHCl}_3$  60:40) to afford pure **TC2** (23 mg; 22 %) as white powder.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  = 7.43 and 7.45 (d, 4H, Ar-H), 7.11 (s, 4H, Ar-H), 5.45 (s, 2H, O- $\text{CH}_2$ -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 5.04 (s, 4H, 2 -O- $\text{CH}_2$ -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 4.28 (t, 2H,  $^3J$  = 7.72, O- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_3$ ), 3.36-3.54 (m, 12H, 3 O- $\text{CH}_2$ -CO-N( $\text{CH}_2$ - $\text{CH}_3$ ) $_2$ ), 1.94-1.97 (m, 2H, O- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_3$ ), 1.04, 1.16 and 1.25 (m, 57 H, O-

CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, 3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub> and Ar-C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) : δ = 167.52 (Ar-O-CH<sub>2</sub>-CO-), 158.01 (ArC-O), 146.92 (ArC-C(CH<sub>3</sub>)<sub>3</sub>), 134.85, 135.57 and 135.96 (ArC-H), 128.50, 129.17 and 130.96 (ArC-S-), 70.28 and 72.69 (Ar-O-CH<sub>2</sub>-), 40.26, 41.56 and 41.78 (O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 34.41 and 34.57 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 31.48, 31.67 and 31.83 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 24.23 (O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 14.52 and 14.89 (O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 13.44 (O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>). ES-MS. (positive mode): mass (m/z) = 1102.5 [M+H]<sup>+</sup>, 1124.5 [M+Na]<sup>+</sup>. Mp = 200 °C.

**5,11,17,23-tetra-*p*-*tert*-butyl-25,26,27-*N,N*-diethylaminocarbonyl-28-ethoxycarbonylthiacalix[4]arene TC3** (cone conformer). To a solution of 0.15 g (0.141 mmol) of **TC1** and 0.011 g (0.08 mmol) of K<sub>2</sub>CO<sub>3</sub> in acetone (5 mL), under nitrogen flux, was added 0.031 mL (0.283 mmol) of ethylbromoacetate. The mixture was refluxed for three days. The solvent was removed under vacuum. To the residue was added CHCl<sub>3</sub> (20 mL) and an aqueous solution of HCl 1N (10 mL). The organic layer was separated, washed with water (3 × 10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by chromatography on silica gel (0.04-0.063 mm from Merck; eluted with heptane / CHCl<sub>3</sub> 60:40) to afford pure **TC3** (81 mg; 50 %) as white powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) : δ = 7.36, 7.52 and 7.64 (m, 6H, Ar-*H*), 7 (s, 2H, Ar-*H*), 4.73, 4.98 and 5.37 (m, 8H, 3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub> and O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>), 4.21 (q, 2H, <sup>3</sup>J = 7.32, O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>), 3.21 and 3.41 (m, 12H, 3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 1.10, 1.18, 1.25, 1.28 and 1.31 (m, 57H, 3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>, Ar-C(CH<sub>3</sub>)<sub>3</sub> and O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) : δ = 166.43 and 167.29 (Ar-O-CH<sub>2</sub>-CO-), 156.03 and 158.44 (ArC-O), 149.82 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 136.80, 136.99 and 137.02 (ArC-H), 128.32, 130.43 and 130.94 (ArC-S-), 71.74 and 75 (Ar-O-CH<sub>2</sub>-), 61.74 (O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>), 40.44, 41.44 and 41.92 (O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>), 34.83 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 31.32 and 31.52 (Ar-C(CH<sub>3</sub>)<sub>3</sub>), 14.72 (O-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>3</sub>),

13.40 and 14.57 (3 O-CH<sub>2</sub>-CO-N(CH<sub>2</sub>-CH<sub>3</sub>)<sub>2</sub>). ES-MS. (positive mode): mass (m/z) = 1146,4 [M+H]<sup>+</sup>, 1168,4 [M+Na]<sup>+</sup>. Mp = 215 °C.

**Complexation.** The stability constants K defined as the concentration ratio [ML] / ([M][L]) (where M = cation and L = ligand) were determined at 18 °C, in acetonitrile or a mixture of acetonitrile/water (3v/v) by UV absorption spectrophotometry. The spectra were recorded on a Shimadzu UV-2401-PC. The procedure consisted in adding increasing amounts of metallic salts (5.10<sup>-4</sup> M) to a solution of **PC1-3** ([**PC1-3**] = 5.10<sup>-5</sup> M). The metal salts used were chlorides, perchlorates, nitrates or trifluoroacetates according to their solubility in the solvents used. The following salts were used in pure acetonitrile : Cd(ClO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O, CF<sub>3</sub>COOAg, Zn(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, Cu(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O, PdCl<sub>2</sub>, (CF<sub>3</sub>COO)<sub>2</sub>Hg. In a mixture of acetonitrile/water (3v/v) the following salts were used : Pb(NO<sub>3</sub>)<sub>2</sub>, NiCl<sub>2</sub>.6H<sub>2</sub>O, Hg(ClO<sub>4</sub>)<sub>2</sub>.4H<sub>2</sub>O.

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Table 1. Stoichiometry of Metal-Ligand complexes.

	$\text{Cd}^{2+}$	$\text{Pd}^{2+}$	$\text{Pb}^{2+}$	$\text{Hg}^{+}$	$\text{Hg}^{2+}$	$\text{Zn}^{2+}$	$\text{Cu}^{2+}$	$\text{Ni}^{2+}$	$\text{Ag}^{+}$
<b>TC1</b>	ML	ML	ML	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	ML	ML
<b>TC2</b>	<i>a</i>	ML	ML	<i>b</i>	<i>a</i>	ML	<i>a</i>	ML	ML
<b>TC3</b>	ML	ML	ML	<i>b</i>	ML	ML	<i>a</i>	<i>a</i>	$\text{ML}_2$

(a)  $\text{M}_x\text{-L}_y$  complexes are observed. (b) no complexation was observed.

Table 2. Stability constants of (1:1) Metal-Ligand complexes. LogK ( $\lambda$ (nm)).

	$\text{Cd}^{2+}$	$\text{Pd}^{2+}$	$\text{Pb}^{2+}$	$\text{Hg}^{2+}$	$\text{Zn}^{2+}$	$\text{Ni}^{2+}$	$\text{Ag}^{+}$
<b>TC1</b>	8.04 (281.5)	2.69 (244.5)	4.51 (281.5)	-	-	4.42 (278)	4.14 (281)
<b>TC2</b>	-	3.21 (242.5)	4.76 (294.5)	-	4.28 (236)	4.07 (284)	3.78 (294)
<b>TC3</b>	4.20 (283)	3.21 (242.5)	2.82 (284.5)	4.61 (282.5)	2.28 (292)	-	-

It should be noted that these values are approximations of the ligand affinity. Indeed, error in our calculations due to the uncertainties involved in  $\epsilon$  determination and concentration of the solutions cannot be neglected.